



Utilisation of a multitubular reactor system for parallel screening of catalysts for ring opening of decalin in continuous mode



Kalle Arve^{a,*}, Päivi Mäki-Arvela^a, Kari Eränen^a, Marja Tiitta^b, Tapio Salmi^a, Dmitry Yu. Murzin^a

^a Laboratory of Industrial Chemistry and Reaction Engineering, Process Chemistry Centre, Åbo Akademi University, 20500 Turku/Åbo, Finland

^b Neste Oil, P.O. Box 310, FIN-06101 Porvoo, Finland

HIGHLIGHTS

- Catalysts activity, selectivity and stability were studied in a continuous reactor for ring opening of decalin.
- Stable conversion in continuous operation mode was achieved.
- Catalyst deactivation was found to originate mainly due coking.
- Highest selectivity towards ring opening products was recorded over a Pt/Ir–silica–alumina catalyst.

ARTICLE INFO

Article history:

Available online 4 July 2013

Keywords:

Decalin
Ring opening
Continuous reactor
Catalyst deactivation

ABSTRACT

The activity and selectivity of Pt/Beta, Pt/Ir-Beta/alumina and Pt/Ir-Beta/silica was investigated in the ring opening of decalin at 250–350 °C in the presence of hydrogen. Time on stream experiments were performed in a special tailor made reactor system for advanced screening for catalytic three-phase reactions in continuous mode to study the decalin conversion, selectivity towards ring opening products and catalyst deactivation. The results from the activity tests were correlated to the catalyst properties. Conversion of decalin was found to be the highest over the Pt/Beta catalyst, which was the most acid catalyst. However, the highest selectivity towards the ring opening products was recorded over less acidic Pt/Ir-Beta/silica catalyst at 300 °C and 40 bar H₂. The experimental results indicated that under conditions optimised for ring opening selectivity (300 °C, 40 bar H₂) all the tested catalysts were slightly deactivated with time on stream. However, only when the temperature was increased to 325 °C severe carbon deposition on the tested catalysts were found. Based on the coke analysis mainly naphthenes and olefins caused deactivation, which lead to changed product selectivity.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The increasing environmental awareness during the past few decades has been the main driving force for more stringent environmental legislation. The specifications on fuels, such as gasoline and diesel, have followed this general trend and resulted in significant modifications and development of refinery technologies. The dramatically increased consumption [1] of diesel into the most wanted transportation fuel has let to a huge demand to increase its production capacity and quality. To improve the quality of diesel sulphur and aromatic content can be reduced by using existing commercial technology, *i.e.* hydrocracking and hydrotreatment [2]. Such treatment result directly in lower particulate matter (PM) content in the exhaust and also lowers the density of diesel fuel. However, these technologies are not very efficient to increase the

cetane number (CN) of the fuel as the CN of naphthenes is initially low. Thus, opening at least one of the naphthenic rings is essential to obtain satisfactory cetane numbers to obtain high quality diesel [2–5]. Furthermore, the resulting decreased density of the ring opened feedstock will provide higher volume.

Ring opening of naphthenes can principally be performed by two different catalytic mechanisms, namely those being promoted on active metal sites (hydrogenolysis) and those being promoted on acidic sites (cleavage of endocyclic C–C bonds) of which catalytic ring hydrogenation followed by ring opening is to prefer [6]. The catalytic ring hydrogenation followed by selective ring opening results in different hydrocarbons of which alkanes with as high as possible carbon number are most preferable. Platinum group metals (platinum, iridium, ruthenium and rhodium) supported on acidic micro- or mesoporous metal oxides as well as various metal- and oxycarbides have been reported for catalytic ring opening of naphthenes reaction [7–18].

Activities and selectivities of catalytic ring opening using model compounds over solid acids and metal modified zeolites in batch

* Corresponding author. Tel.: +358 22154437.

E-mail address: karve@abo.fi (K. Arve).

reactors have been reported for instance by Kubička et al. [11,12] among many others. In addition, studies reporting catalytic data for the industrially relevant continuous operation mode for ring opening reaction have been recently published [16–18].

However, hydrotreating of naphthenes does not only lead to the formation of the desired ring opening products. As ring opening products can be formed directly from decalin (Fig. 1) the main route is via isomers. Ring opening products formed from isomers have all a C_{10} structure according to their classification and typical products are for instance methyl-cC6, ethyl-cC6, propyl-cC6 or butyl-cC6. Furthermore, depending on the reaction conditions these molecules will be further cracked to shorter hydrocarbons, which degrade the amount of diesel quality components in the product stream being thus highly unwanted compounds (Fig. 1). In principle, the yield of the ring opening products is a trade off between unreacted naphthenes and cracking products. Therefore, the process conditions, *i.e.* temperature and pressure need to be optimised according to the catalyst in use. Other important issues affecting the catalytic ring opening reaction are activity, selectivity and rates of deactivation of the applied catalysts. So far the reported selectivities towards ring opening products for existing catalysts have generally been rather low, approximately 15–30% or less at conversion levels above 90% [11,12,16–18], in a temperature range 280–310 °C. Higher selectivity can be achieved at lower temperatures at the cost of decreased conversion of naphthenes whereas increasing the reaction temperature will result in a rapid decrease of ring opening products and increase of cracking products. At optimised conditions ring opening catalysts show, however, stable performance in time on stream experiments. In addition, selectivities as high as 60% over Ir/H-Beta catalyst have been reported by Kubička et al. [19].

The majority of reported data for the ring opening of decalin were obtained in batch mode [11,12,19]. For industrial applications continuous mode would be preferable. Such studies have been reported although scarce by Ardakini and Smith [16], Rabl et al. [18] and Mouli et al. [21]. Of these reports Ardakini and Smith [16] have grouped products with carbon number in the range C_7 – C_{10} among ring opening products. This differs from the grouping made in other studies, including ones by our group, where only C_{10} molecules are classified as ring opening products and compounds with lower carbon number are classified as unwanted cracking products. Thus direct comparison between results presented by Ardakini and the other authors should not be made.

Selective catalytic ring opening of polynuclear aromatic hydrocarbons is usually studied with model hydrocarbons, such as decalin or tetralin. The reported ring opening products from decalin or tetralin are naphthenes C_{10} having one remaining ring [12,19–23].

The need for diesel fuel is constantly increasing along with the increasing number of diesel vehicles as well as the environmental legislation for diesel quality is strictening. Therefore, industry must develop new ways to meet these challenges. Catalytic ring opening of middle distillates is a promising option for achieving environmentally better diesel with higher cetane number [3,10,24–28]. Thus, in this paper the activity and selectivity of Pt/Beta, Pt/Ir-Beta/silica and Pt/Ir-Beta/alumina catalysts on the ring opening of decalin under industrial conditions using a tailor made fixed bed reactor system was studied. In addition, the effect of contact time and reaction temperature on the ROP selectivity and catalyst deactivation was investigated. Furthermore, the nature of the formed coke on the catalyst surface was qualitatively analysed.

2. Experimental

2.1. Reactor system

A reactor system consisting of six parallel tube reactors was constructed in house (Fig. 2). Essential features of this reactor system are continuous operation, possibility to use two or three phases, realistic catalyst particle sizes, ability to perform parallel screening of various catalysts as well as study temperature effects, recognising of catalyst deactivation and capability to run transient and steady state operations. The inner diameters of the reactor tubes were 10 mm and the catalysts were placed into the reactors by using glass wool and metal nets as supports for the catalyst beds. The liquid was pumped into the system by using an HPLC-pump (Agilent 1100 Quaternary pump). An equal liquid-phase distribution between the reactors was obtained by using calibrated capillary tubes located upstream of each reactor. For introduction of gases, the system is equipped with four mass flow controllers (Brooks 5850S) with different flow ranges to be able to utilise a broad range of flow rates and mixtures. The main gas flow was divided into six equal flows by using the same type of calibrated capillaries as for the distribution of the liquid. In addition, a back-pressure controller (Brooks 5866), located downstream of the reactors, was used to maintain system pressure. The reactors were surrounded by separate aluminium blocks, which were heated by cartridge heaters. The temperature of each reactor was controlled separately by using temperature controllers (CAL Controls 9500P) and the temperature was recorded inside the catalyst bed by using internal thermocouples. Isothermal conditions were maintained in all the reactors. The catalyst temperatures in the different reactors were measured with thermocouples inserted in the beds. Online gas samples could be analysed by a GC-MS (Agilent 6890/5973N)

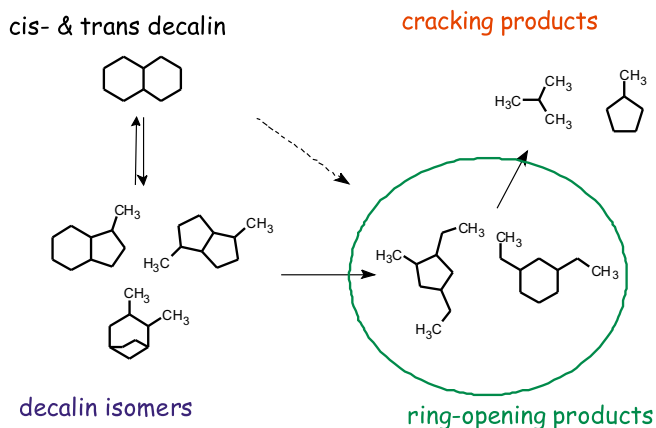


Fig. 1. Schematic view of hydrotreating of decalin leading to ring opening products (ROP) and further to cracking products.



Fig. 2. Picture of parallel reactor system used to study the activities and selectivities of different ring opening catalysts.

Download English Version:

<https://daneshyari.com/en/article/148030>

Download Persian Version:

<https://daneshyari.com/article/148030>

[Daneshyari.com](https://daneshyari.com)